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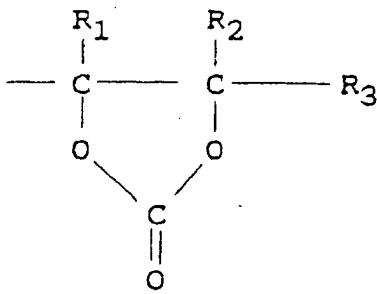
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㉗ Storage stable aqueous emulsions.

㉘ Aqueous emulsions of cyclocarbonate-group containing polymers having a solid content of 5 to 80%, advantageously of 25 to 50%, of cyclocarbonate group containing emulsified polymers which on average bear per macromolecule at least two 2-oxo-1,3-dioxolane-4-yl-groups of general formula

substituted or unsubstituted methyl group, wherein the residues can be identical to each other or different and processes for their manufacture.



as side or end groups
in which

R₁, R₂ and R₃ each stand for a hydrogen atom or a



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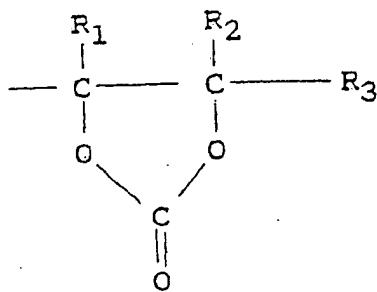
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as side or end groups

in which

R₁, R₂ and R₃ each stand for a hydrogen atom or a substituted or unsubstituted methyl group, wherein the residues can be identical to each other or different and processes for their manufacture.

Description

STORAGE STABLE AQUEOUS EMULSIONS

5

BACKGROUND OF THE INVENTIONField of the Invention

10 The present invention relates to aqueous emulsions of cyclocarbonate group-containing polymers and to a process for their manufacture.

Emulsions according to the invention mean also suspensions.

Description of the Prior Art

15 Stable aqueous emulsions of numerous polymers are known. S. Paul (Surface Coatings, J. Wiley & Sons, 1985) describes for instance aqueous emulsions of epoxy, polyurethane, alkyd and polyester resins.

Aqueous emulsions of functional acrylic and methacrylic polymers are described by G.Y. Tilak in Progress in Organic Coatings, 13 (1985), 333-345. Important functional groups, which can be reacted in the ensuing hardening of the emulsified (meth)acrylic resins, are for instance hydroxyl, carboxyl, amide and glycidyl groups.

20 An interesting functional group is presented by the 2-oxo-1,3-dioxolane group. The introduction of this group succeeds by reaction of epoxy compounds with carbon dioxide (e.g. DE-OS 35 29 263).

Solutions of cyclocarbonate-containing resins in common organic solvents are known. In DE-OS 35 29 263 cyclocarbonate-containing epoxy resins are described which can be present either solvent-free or dissolved in organic solvents. Also cyclocarbonate group-containing acrylic polymers are known. Subject of the European 25 patent application EP 1088 are cyclocarbonate group-containing polymerizates which are prepared by solution polymerization.

In US-PS 29 67 173 processes are described which are suitable for the preparation of cyclocarbonate functional polymer solutions.

30 In contrast to organic solvent-containing polymer systems aqueous emulsions are especially ecologically harmless and are being used to an increasing extent for instance in the areas of coatings, adhesives or sealants. The manufacture of cyclocarbonate group-containing polymers in aqueous media therefore is of great interest, but it is not sufficiently solved within the prior art.

35 US-PS 29 67 173, for example, describes that in the emulsion polymerization of cyclocarbonate group-containing monomer mixtures particulate precipitates are formed and no stable emulsions can be obtained. Also the bibliographical reference V.I. Yeliseyeva in I. Piirma (Ed.) "Emulsion Polymerization", Academic Press, 1982, p. 247 describes difficulties which are encountered on emulsifying in aqueous systems. The cyclocarbonate group-containing monomers exhibit such a strong aprotic polar character (viz. Huls AG, information brochure "Alkylencarbonate", 1985) that until now all the attempts failed to prepare aqueous emulsions.

40 From the prior art results that the known methods for the manufacture of cyclocarbonate group-containing polymers can be applied only to polymerizations in organic solvents, but that they are unsuitable for the manufacture of aqueous emulsions of cyclocarbonate group containing polymers and especially of storage stable aqueous emulsions of such polymers.

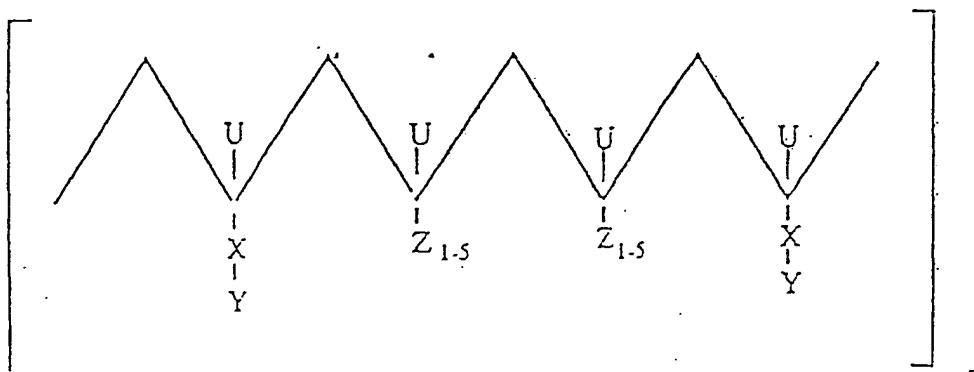
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SUMMARY OF THE INVENTION

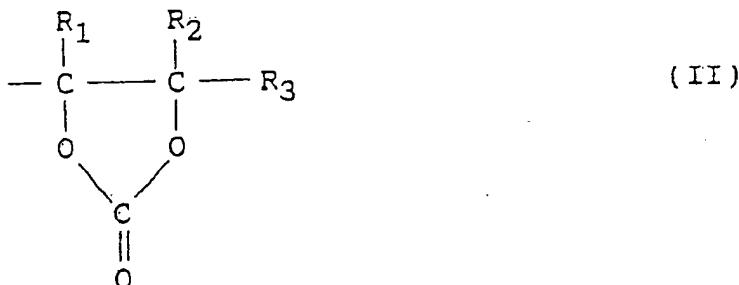
Object of the present invention is to manufacture storage stable aqueous emulsions of cyclocarbonate-group containing polymers.

50 The aqueous emulsions according to the invention remain stable for at least one month in the temperature range of 15 to 30°C and have a polymer content of 5 to 80%, advantageously of 25 to 60%. They contain emulsified polymers which on average bear per macromolecule at least two 2-oxo-1,3-dioxolan-4-yl groups of general formula (II) below.

55 More particularly, according to a first embodiment of the present invention, there is provided an aqueous emulsion, in which it has a solid content of 5 to 80%, advantageously of 25 to 60%, of emulsified polymers in which the main chain consists of partially substituted -CH₂- groups, according to the general formula (I)



wherein U, X, Z₁ to Z₅ have the following meaning:
 U = -H, -CH₃, -COOH, -COOCH₃, -CONH₂, -COO-(CH₂)₁₋₄-X-Y
 Y = 2-oxo-1,3-dioxolan-4-yl groups of general formula (II)



in which

R₁, R₂ and R₃ each stand for a hydrogen atom or a substituted or unsubstituted methyl group, wherein the residues can be identical to each other or different,

Z₁ = -O-C-(CH₂)₁₋₄-, -S-C-(CH₂)₁₋₄-, -O-C-NR-(CH₂)₁₋₄-

where R = H or alkyl,

Z₂ = -COO-(CH₂)₆₋₁₇-CH₃

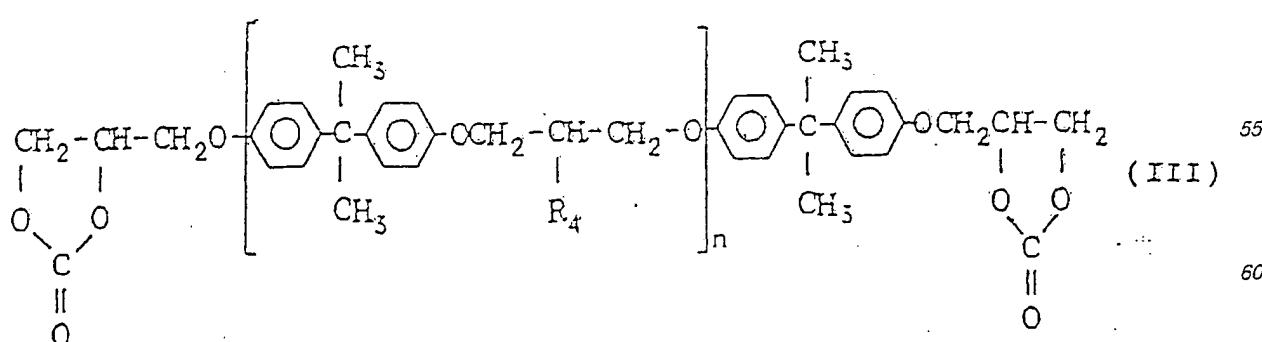
Z₃ = phenyl-, meta-, ortho-, para-substituted alkylphenyl groups

Z₄ = -COOH

Z₅ = -COO-(CH₂)₁₋₄-OH, -COO-(CH₂-CH₂O)₁₋₁₀-CH₂-CH₂-OH

in which at least two groups -X-Y per macromolecule have to be present and the groups Z₁ or Z₂ can be present either alone or Z₁ in combination with Z₂ to Z₅, wherein the sum of the weight portions of the polymerizable starting materials with the groups -X-Y and Z₄ in the emulsified macromolecule must not exceed the value of 70% by weight.

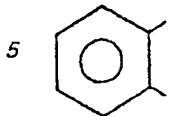
According to a second embodiment of the present invention, there is provided an aqueous emulsion, in which it has a solid content of 5 to 80%, advantageously of 25 to 60%, of emulsified polymers in which the main chain is built according to the general formula (III) and the secondary OH groups are fully or partially substituted by R₄



wherein n stands for a number from 1 to 10 and R₄ is a half ester group of the general formula (IV)

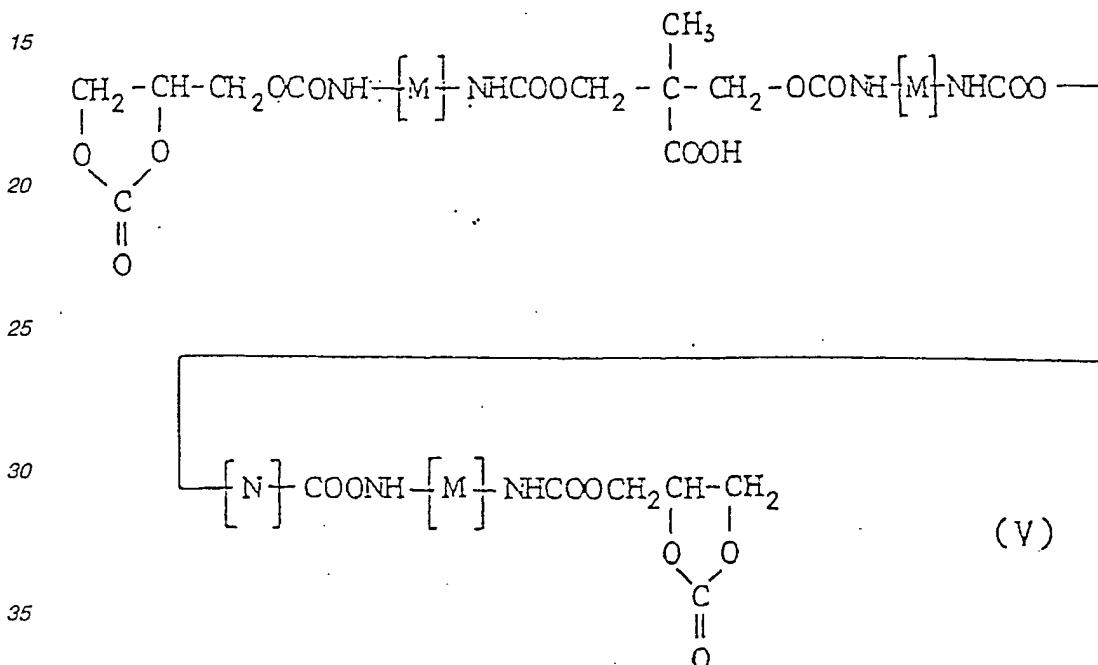
-O-C-B-C-OH (IV)

with B being equal to $-(CH_2)_2-3-$, $-CH=CH-$, or



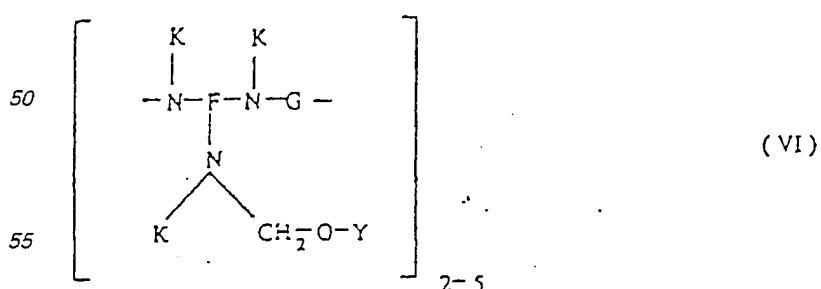
which is fully or partially neutralized with alkali metal ions or with secondary or tertiary amines.

10 According to a third embodiment of the present invention, there is provide an aqueous emulsion, in which it has a solid content of 5 to 80%, advantageously of 25 to 60%, of emulsified polymers in which the main chain is built according to the general formula (V) below:



40 wherein [M] stands for an aliphatic, cycloaliphatic, aromatic or arylaliphatic group with 6 to 20 carbon atoms and [N] is equivalent to a polyalkylene oxide with 0 to 20 repetitive units, to an aliphatic or to a mixed aliphatic-aromatic polyester with a molecular weight of up to 4000 g/mol and wherein the acid groups which are incorporated into the main chain each 400 to 500 molecular weight units are fully or partially neutralized with alkali metal ions or with secondary or tertiary amines.

45 According to a fourth embodiment of the present invention, there is provided an aqueous emulsion, in which it has a solid content of 5 to 80%, advantageously of 25 to 60%, of emulsified polymers in which the straight or branched main chain is built according to the general formula (VI) below:



wherein

F = triazinyl group

$G = -\text{CH}_2\text{-O-CH}_2-$, or $-\text{CH}_2-$.

$K = -H$, $-\text{CH}_2\text{COOH}$, or $-\text{CH}_2-\text{O}-\text{R}$ (with $\text{R} = \text{H}$, alkyl with 1 to 4 carbon atoms)

$Y = 2\text{-oxo-1,3-dioxolan-4-yl}$ group according to general formula (III)

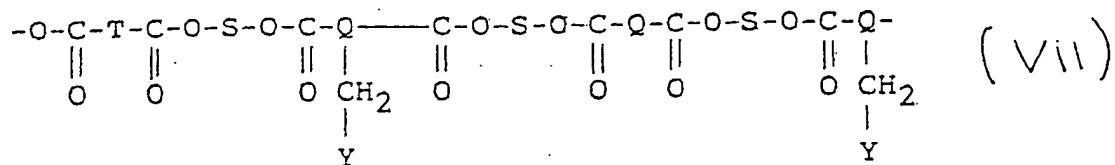
in which at least two groups Y per macromolecule and not more than 2 groups Y per triamino-triazine unit have to be present.

According to a fifth embodiment of the present invention, there is provided an aqueous emulsion, in which it

has a solid content of 5 to 80%, advantageously of 25 to 60%, of emulsified polymers in which the straight or branched main chain is built according to the general formula (VII)

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wherein

T = $-(CH_2)_{2-10}-$, $-(CH_2-CHR)_{1-5}-$, or $-CH=CR-$ (with R = H, alkyl, ortho-, meta-, para-substituted phenyl groups)

30

S = $-(CH_2)_{2-12}-$, $-(CH_2-CHR-O)_{1-20}-$, or $-CR_{4-m}[(CH_2-CHR-O)_{1-20}]_m$ with R = H or alkyl, and m = 1 to 4

Q = tri- or tetrasubstituted phenyl groups with one or two additional $-COOH$ groups

Y = 2-oxo-1,3-dioxolan-4-yl group according to general formula (II)

in which at least 2 groups Y per macromolecule have to be present and in which the free acid groups in emulsion are fully or partially neutralized with alkali metal ions or with secondary or tertiary amines:

35

Object of the present invention is also a process for the manufacture of such emulsions by emulsion polymerization in water of an olefinic unsaturated polymerizable compound with at least one cyclocarbonate group of general formula (II), and emulsion copolymerization in water of a mixture of olefinic unsaturated polymerizable compounds of which at least one contains at least one cyclocarbonate group of general formula (II).

40

Object of the present invention is further a process for the manufacture of storage stable aqueous emulsions of cyclocarbonate group-containing polymers, in which solvent-free and solvent-containing polymers which on average bear per molecule at least two 2-oxo-1,3-dioxolan-4-yl residues of general formula I, are emulsified in water.

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In a preferred embodiment, the present invention provides a process for the manufacture of an aqueous emulsion of emulsified polymers; in which polymers are manufactured by aqueous emulsion copolymerization of:

a) 1 to 60% by weight of a polymerizable compound containing group (II) with

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b) 20 to 95 weight % of non-functional esters of acrylic or methacrylic acid in the alcohol residue and optionally

c) 5 to 75 weight % of aromatic vinyl compounds

d) 1 to 40 weight % of hydroxyl group bearing α , β -ethylenic unsaturated compounds unsaturated compounds

e) 1 to 20 weight % of α , β -unsaturated mono- or dicarboxylic acids

55

f) 1 to 40 weight % of polar-aprotic acrylic or methacrylic monomers with 1 to 12 carbon atoms and at

least one nitrile- or dialkylamino group in the side group, wherein the sum of the weight portions a) and f) must not exceed the value of 70 weight % in the polymer, with an ionic, preferably anionic emulsifier of a high hydrophilic value and a water-soluble initiator or a redox-initiator system in the temperature range between 0 and 70°C.

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Object of the present invention is also a coating material containing one or more aqueous emulsions with or without usual additives.

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DETAILED DESCRIPTION OF THE INVENTION

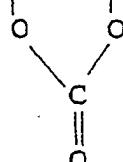
5 For the manufacture of storage stable aqueous emulsions of cyclocarbonate group-containing polymers according to the invention by the process of emulsion polymerization compounds are suitable as starting materials which beside an unsaturated polymerizable function have at least one 2-oxo-1,3-dioxolan-4-yl-group, especially

10 a) derivatives of unsaturated monobasic acids such as for instance acrylic, methacrylic or crotonic acid, e.g.

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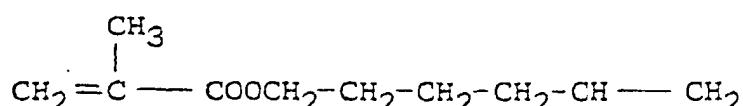


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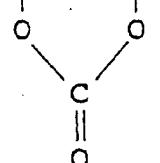


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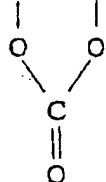


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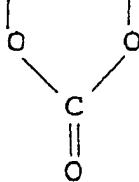
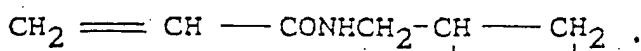
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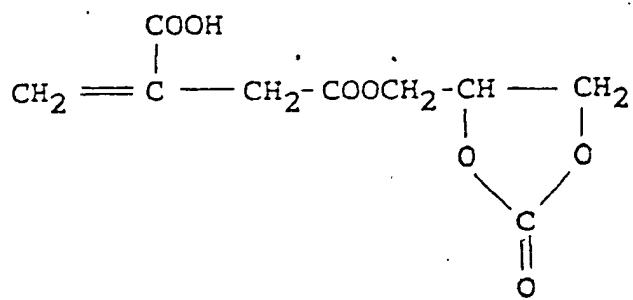
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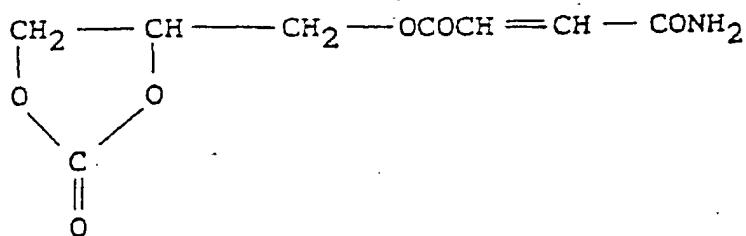
60 b) derivatives of polybasic unsaturated carboxylic acids such as for instance maleic, fumaric or itaconic acid, e.g.

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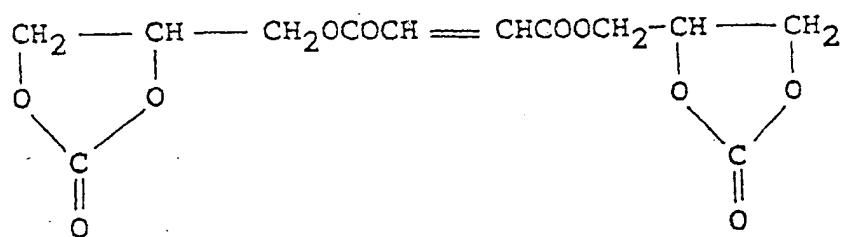
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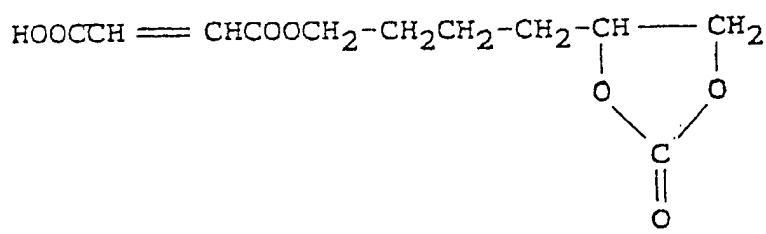
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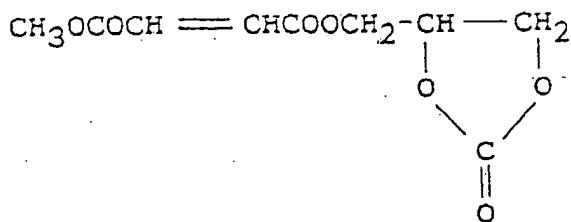
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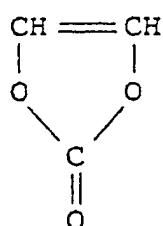
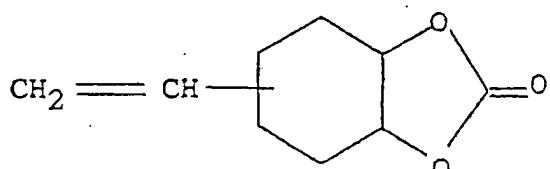
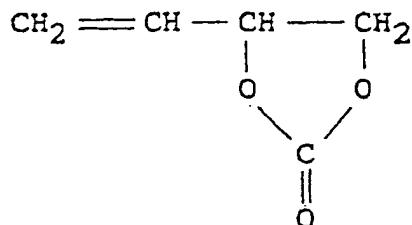


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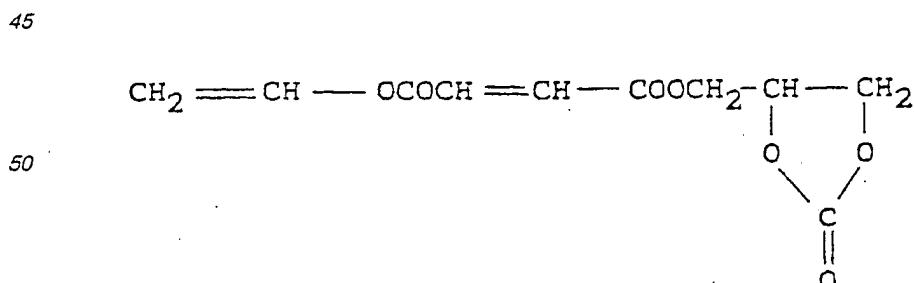
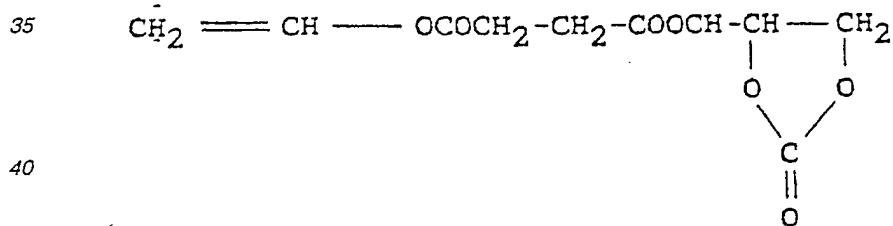
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c) ethylenic derivatives, e.g.



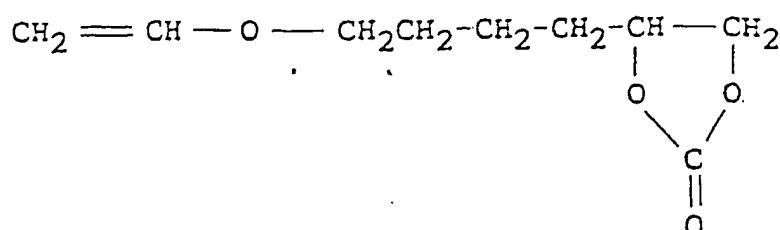
d) vinylesters which in the acidic residue bear at least one 2-oxo-1,3-dioxolan-4-yl-group, e.g.



e) vinylethers, e.g.

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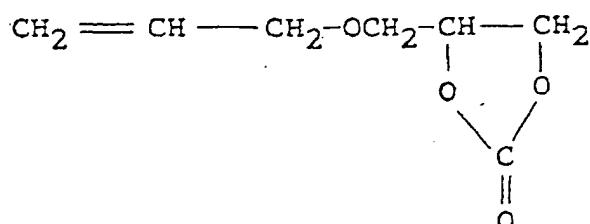
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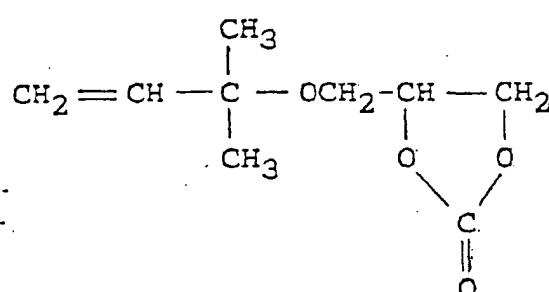
f) derivatives of mono- or polyfunctional unsaturated alcohols, e.g.



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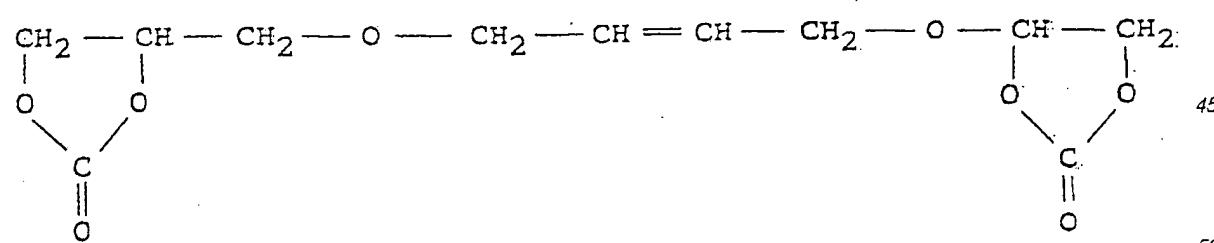
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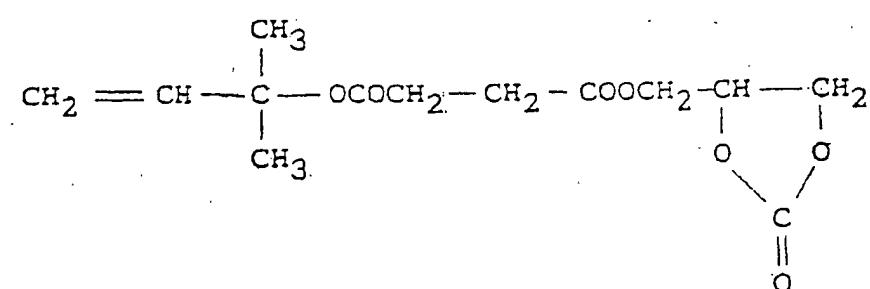
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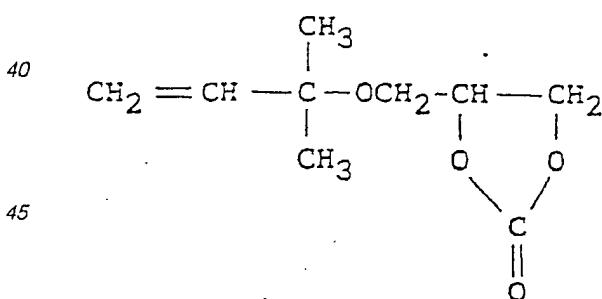
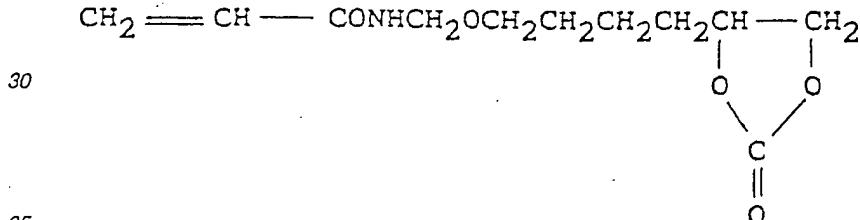
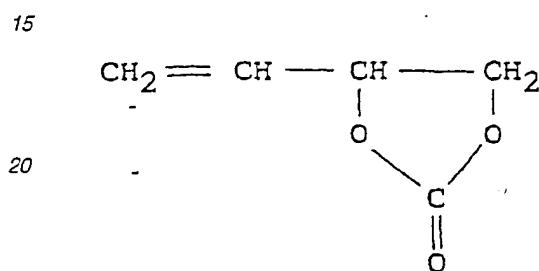
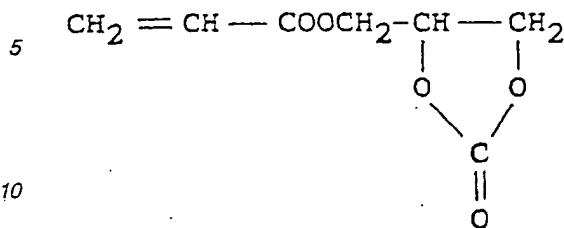


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Such substances can be transferred by aqueous emulsion polymerization into polymers with unchanged: 65

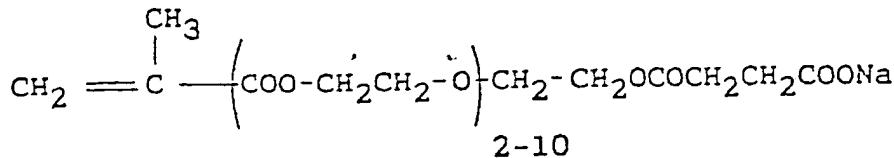
cyclocarbonate functions. For this purpose either single cyclocarbonate monomers, e.g.



50 or their copolymers with one another or advantageously in combination with one or more of the common vinyl-, diene- or acrylmonomers or comparable compounds (e.g. esters of maleic acid) are used.

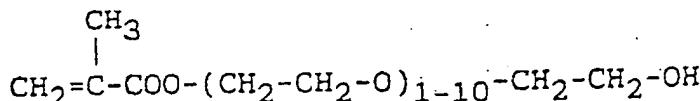
Especially advantageously, styrene, vinyltoluene, acrylic and methacrylic acid and their esters with aliphatic, cycloaliphatic and arylaliphatic alcohols with 1 to 18 carbon atoms, alkylaminoalkylacrylates, as e.g. diethylaminoethylmethacrylate, acrylonitrile or ethylenic unsaturated monomers with OH groups in the side chain can be polymerized with monomers which bear at least one 2-oxo-1,3-dioxolan-4-yl group.

The process according to the invention for the manufacture of storage stable aqueous emulsions of cyclocarbonate group-containing polymers by the principle of emulsion polymerization or emulsion copolymerization can be carried out either without emulsifier or in presence of an emulsifier. Suitable are numerous generally known emulsifiers (e.g. McCutcheon, "Detergents and Emulsifiers", Allied Publishing Co., New Jersey, 1984) of as well anionic, cationic and non-ionic nature. Especially interesting here are emulsifiers which have a polymerizable function as they can be incorporated into the polymer, e.g.



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or as example for a class of polymerizable non-ionic emulsifiers:¹⁰



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The process according to the invention for the manufacture of storage stable aqueous emulsions of cyclocarbonate group-containing polymers by the principle of emulsion polymerization is based upon the radical polymerization in aqueous emulsion. The polymerization initiators needed therefor can be water insoluble or advantageously water soluble. Radicals which start the emulsion polymerization can be generated for instance thermically or by a redox reaction. Suitable substances are e.g. peroxide compounds such as hydroperoxides, peroxides, peracid esters, furthermore azo compounds or redox systems. Several substances of the mentioned classes are known as polymerization initiators (e.g. F. Runge and E. Taeger, "Einführung in die Chemie und Technologie der Kunststoffe", Akademie-Verlag Berlin, 1976). Single initiators of the mentioned groups as well as mixtures of several of such compounds can be used in the process according to the invention.

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The amounts of the particular reaction components in the process according to the invention can be varied in a wide range, so that the polymer content of the obtained emulsions is between 5 and 80%, advantageously between 25 and 60%, and more advantageously between 30 and 40%.

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The emulsion polymerization by the process according to the invention can be carried out within a wide temperature range. Depending upon the activity of the used initiator system and the used emulsifiers it can take place at a temperature between 0° and 100°C, advantageously between 20° and 80°C. An addition of small amounts of organic solvents can have a favorable effect upon the emulsion polymerization for the manufacture of storage stable aqueous emulsions of the present invention, especially if the obtained aqueous emulsion is applied to coatings or paints. Usually the emulsion polymerization is done free of solvents.

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The emulsion polymerization of the present invention can be carried out with an addition of other additives, e.g. emulsion stabilizers, chain transfer agents, buffer systems, detergents, defoamers, conservation agents. In this respect the emulsion polymerization according to the present invention does not differ from the known processes of emulsion polymerization (e.g. I. Piirma, (Ed.), "Emulsion Polymerization", Academic Press, 1982).

40

The storage stability of the aqueous polymer emulsions of the present invention can be influenced advantageously by polymerizing in of monomers which have acid or basic groups respectively, e.g. acrylic or methacrylic acid or dimethylaminoethyl-methacrylate. However, also without incorporation of such monomers, aqueous emulsions of cyclocarbonate group-containing polymers can be obtained by the process according to the invention which exhibit excellent storage stability over several months.

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An especially interesting variation of the process according to the invention for the manufacture of stable aqueous emulsions of cyclocarbonate group-containing polymers with regard to the ensuing application of the emulsions according to the invention is, if desired, beside one or more cyclocarbonate containing monomers and other customary monomers which can be used in an emulsion polymerization in water, substances with a basic or acidic character are polymerized in (e.g. substituted aminoalkylacrylates and acrylic acids). In this way storage stable aqueous emulsions can be manufactured which after complete or partial neutralization result in polymers which are electrodepositable and can be used as electrodeposition coatings.

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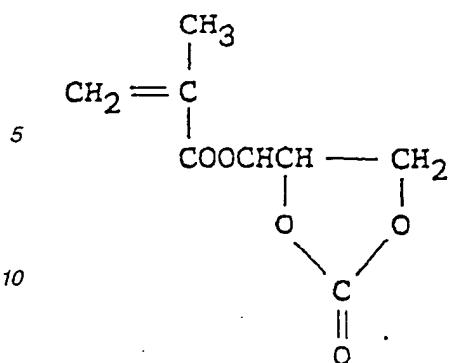
It is also possible, however, that polymers which on average contain at least two cyclocarbonate residues of the general formula I per macromolecule as side or end groups, can be emulsified in water. The polymers to be emulsified can be present free of solvent or solvent-containing and can have a quite variable structure.

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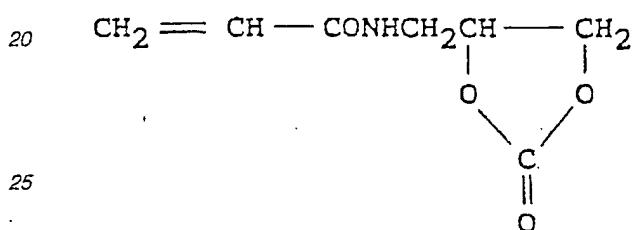
A group of polymers which can be transferred into storage stable emulsions by emulsification in water are substances which are obtained by polymerization of olefinic unsaturated monomers while at least one of the monomers participating in the polymerization has at least one cyclocarbonate function. The following monomers can be transferred into polymers and afterwards can be processed into storage stable emulsions by emulsification in water.

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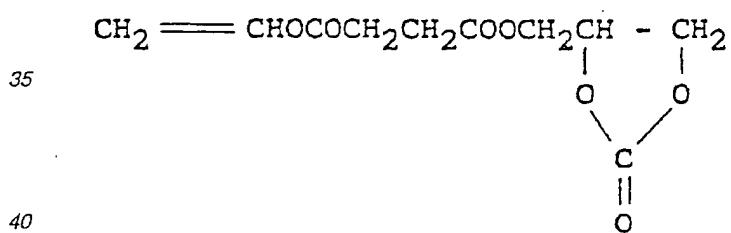


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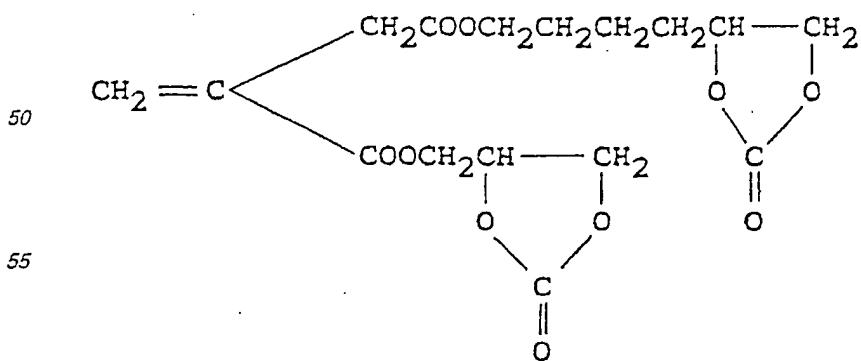
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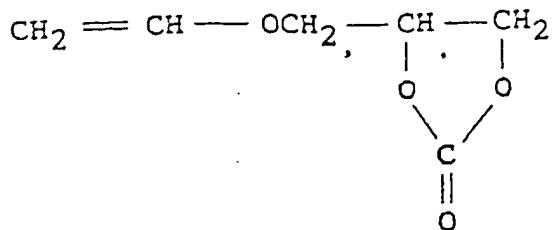
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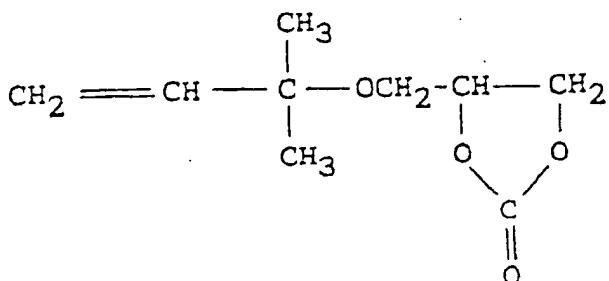
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One of such substances can be polymerized with itself or several with themselves as well as together with all other polymerizable compounds.

Several classes of polymers can be modified with cyclocarbonate groups after their synthesis by a polycondensation or polyaddition process. This can be effected by catalyzed reaction of glycidyl groups with CO_2 according to DE-OS 35 29 263 or by reaction with suitable cyclocarbonate compounds, e.g. with hydroxymethylcyclocarbonate. The thus-modified polymers can be transformed into a storage stable emulsion by emulsifying in water and possibly by removal of a solvent. For this acidic or basic groups are needed which are completely or partially neutralized before or during the emulsifying. Important polymer classes which can be modified with cyclocarbonate groups and transformed subsequently into an aqueous emulsion are epoxy resins, polyurethane resins, melamine resins and polyester resins.

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Another group of polymers which can be transferred into storage stable emulsions by emulsifying in water are substances which are prepared by polycondensation, e.g. epoxy, polyurethane, urea/melamine or alkyd/polyester resins.

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Thus commercial epoxy resins (e.g. from bisphenol A / epichlorohydrin) can be converted according to DE-OS 35 29 263 into cyclocarbonate-modified polymers II as in Reaction Scheme (1).

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Reaction Scheme 1

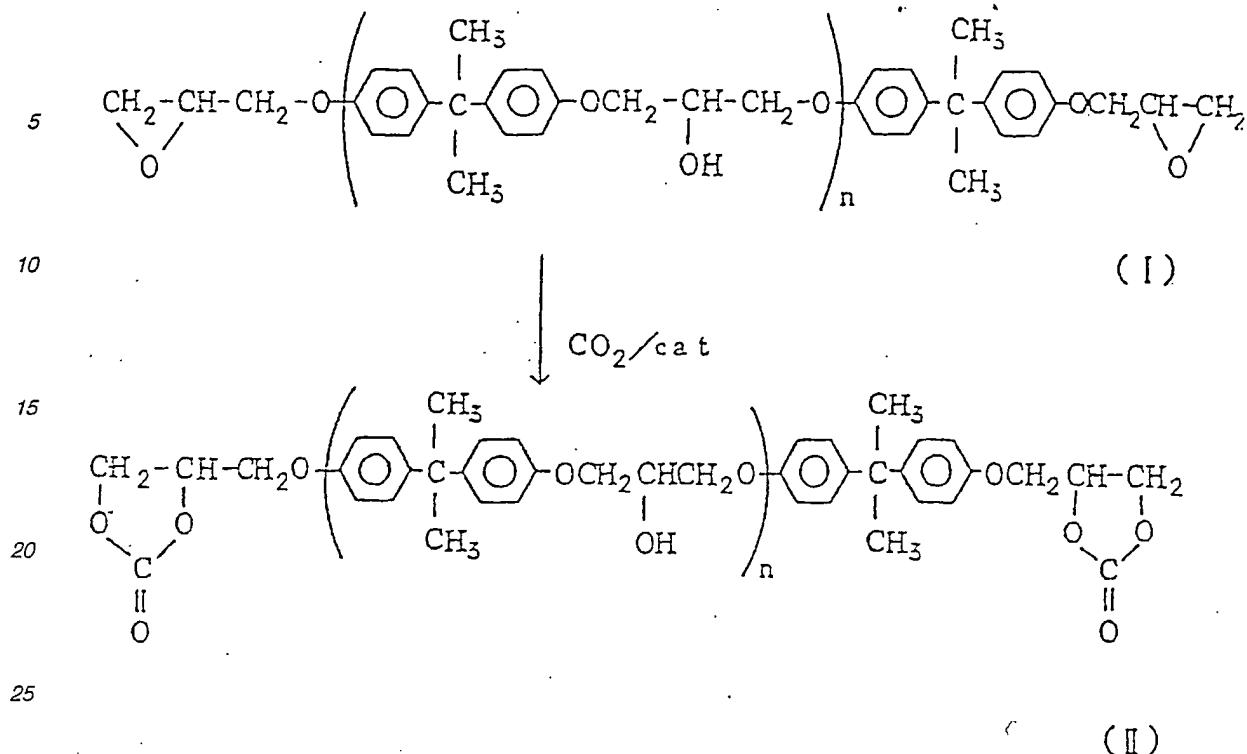
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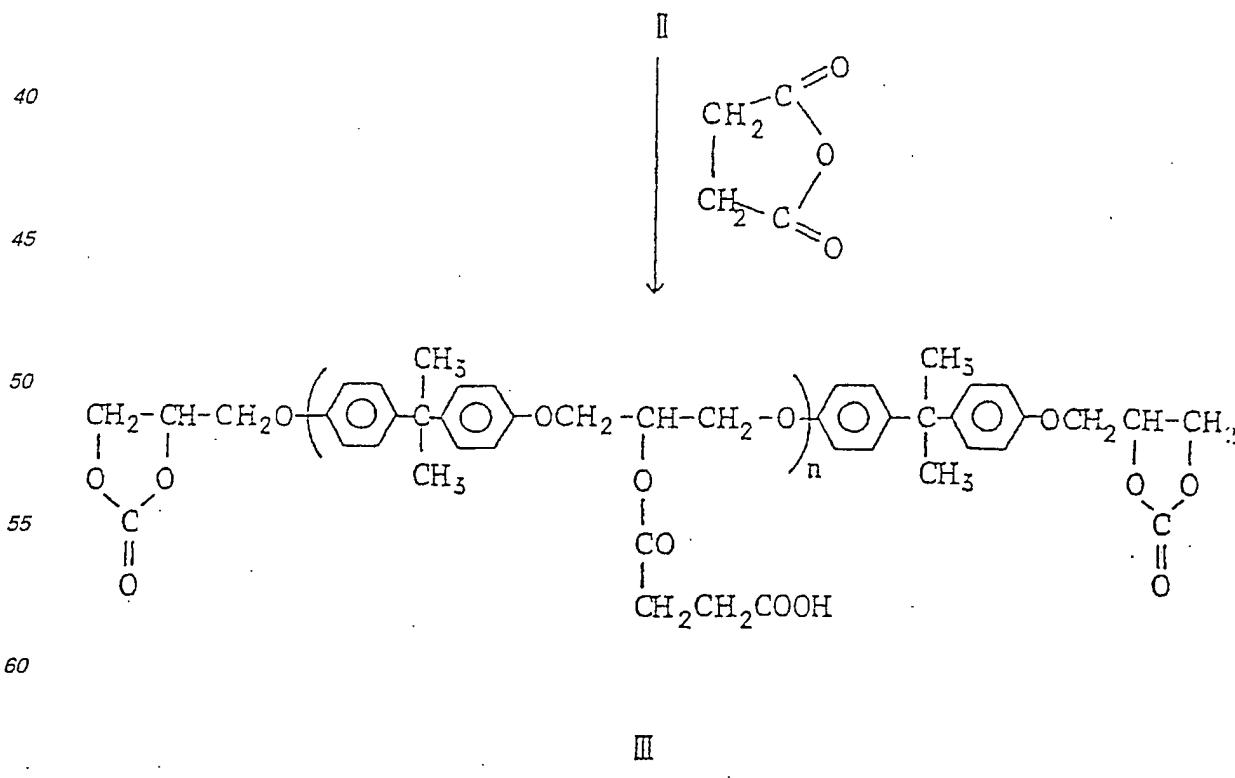
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30 The thus-obtained substances II can be emulsified in water with the usual additives (emulsifiers, protective colloids, etc.) and by applying shearing forces. The bis-cyclocarbonate-epoxy resins II contain one or more secondary hydroxyl groups, which can be esterified with a dicarboxylic acid, e.g. maleic, succinic, glutaric or phthalic anhydride, partially or completely, which is shown in Reaction Scheme (2).

35 Reaction Scheme 2



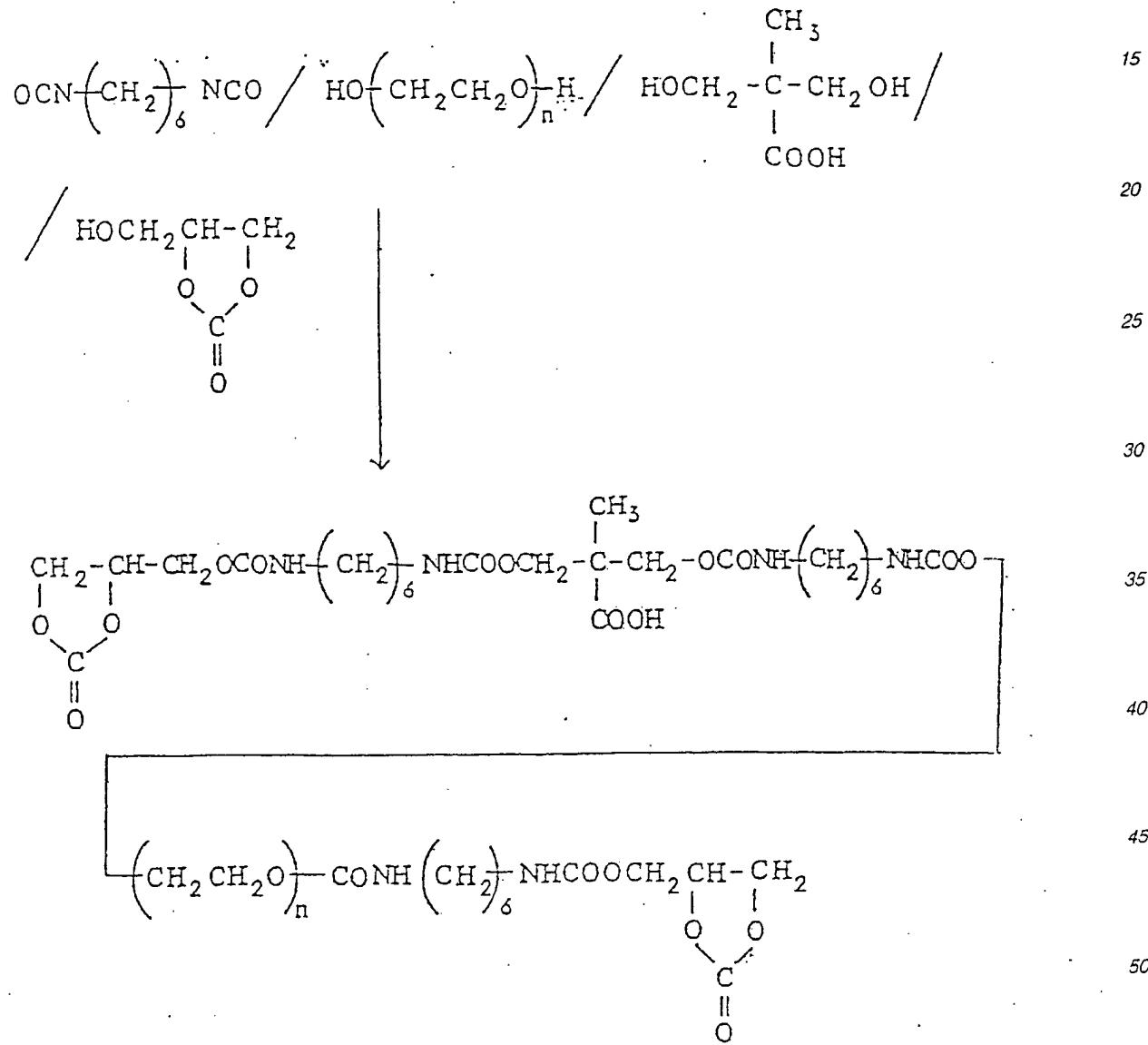
The cyclocarbonate group-containing, with succinic anhydride modified epoxy resins depicted in formula (III) can well be transformed, possibly with partial or complete neutralization with a suitable base, advantageously with a tertiary amine, into storage stable emulsions according to the present invention. Such emulsion are excellently suited as binders for electrodepositable coatings.

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Another group of polymers which can be transferred into storage stable aqueous emulsions or dispersions by emulsifying in water are cyclocarbonate group-containing polyurethanes. They can be obtained for instance from di- or polyisocyanates and suitable polyols and cyclocarbonate-group containing mono-functional alcohols, e.g. according to Reaction Scheme (3).

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Reaction Scheme 3:



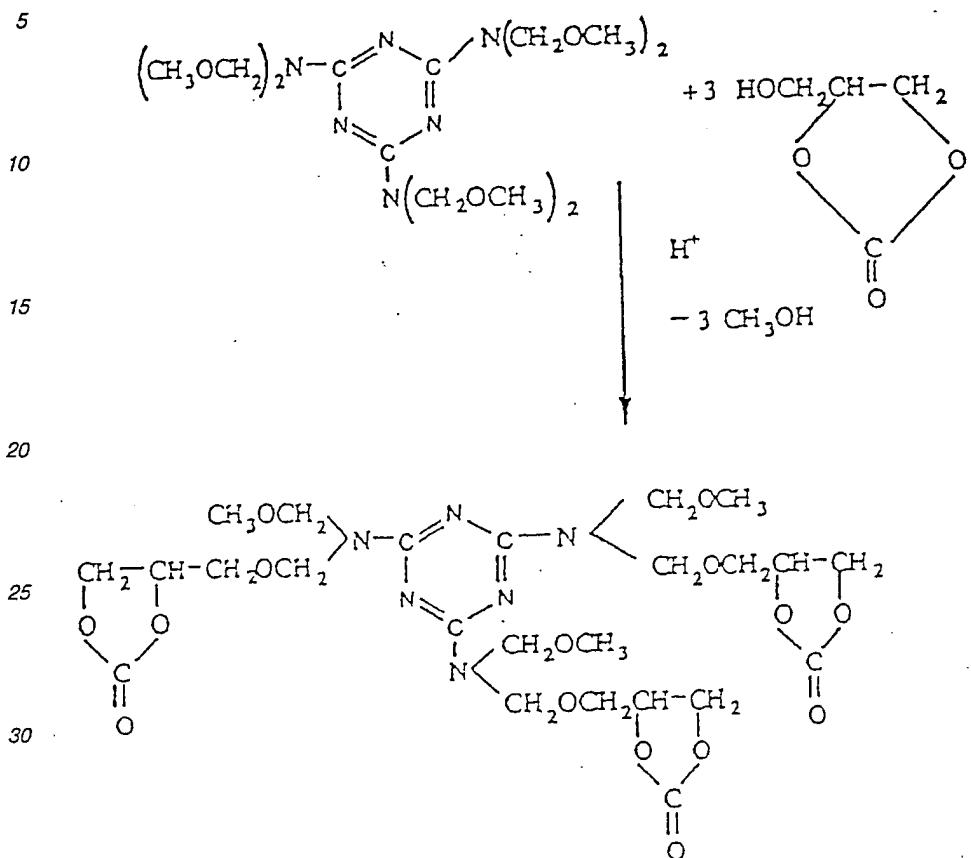
The oligo- or polyurethanes with cyclocarbonate groups synthesized according to Reaction Scheme (3) can be transferred, possibly with partial or complete neutralization, by a suitable base without difficulties into storage stable aqueous emulsions or dispersions according to the present invention. The obtained aqueous emulsions can be used advantageously for the manufacture of coatings, among them electrodepositable paints.

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Cyclocarbonate group-containing urea or melamine resins are suited also for the manufacture of storage stable aqueous emulsions. The cyclocarbonate groups can be introduced into common commercial amino-formaldehyde resins which are etherified with a volatile alcohol (e.g., methanol or butanol), for example, by transesterification, which is depicted by Reaction Scheme (4) schematically for the melamine resin Cymel 303 (American Cyanamide Co.) and (4-hydroxymethyl)-2-oxo-1,3-dioxolane:

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Reaction Scheme 4



The thus-obtained products, which undergo an acid-catalyzed condensation reaction to a certain extent during the transesterification usually can well be emulsified in water similar to the common commercial amino resins.

40 Polyesters, manufactured from aliphatic di- and polycarboxylic acids with 2 to 10 carbon atoms in the chain-
 or their anhydrides, from unsaturated cyclic or aromatic anhydrides and from aliphatic di- and polyols
 according to the common polycondensation processes as described, e.g., by T. C. Patton in "Alkyd Resin
 Technology", Interscience Publishers, New York, London 1962 and which have an acid number exceeding 5
 mg KOH/g polymer, can be modified with suitable OH-functional cyclocarbonate compounds, as e.g.,
 hydroxymethylcyclocarbonate, by partial esterification of the free acid groups and can be emulsified in water
 45 after partial or complete neutralization of the remaining acid groups with alkali metal hydroxides, secondary or
 tertiary aliphatic or aromatic amines, by applying shearing forces and possibly by removal of a solvent. This
 procedure is depicted schematically in Reaction Scheme (5).

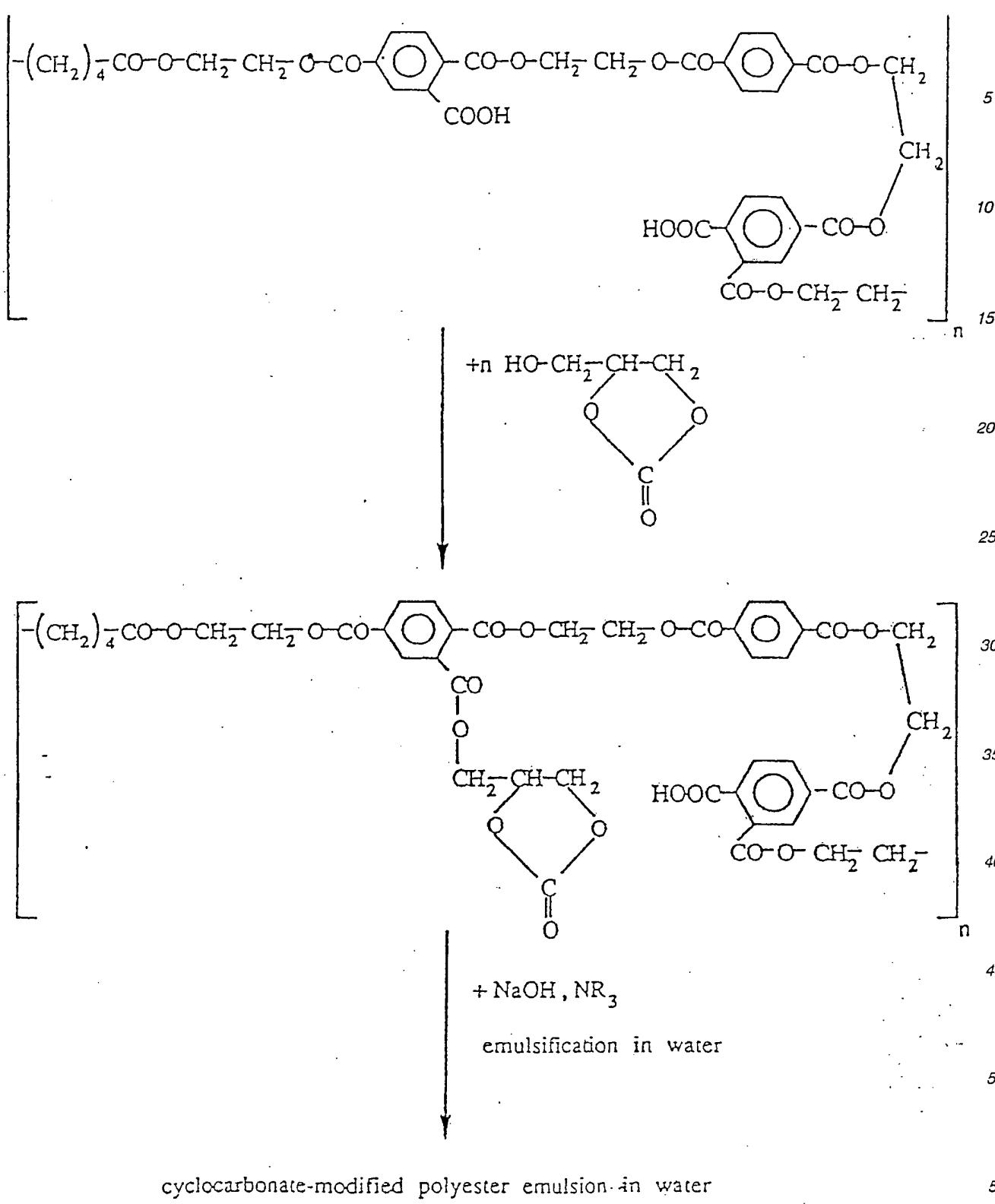
Reaction Scheme 5

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Obviously also alkyd resins, manufactured from triglycerides, cyclic anhydrides, polycarboxylic acids and other diols or polyols, can be modified and emulsified in a similar way as long as they have a sufficient number of free acid groups.

The following examples explain the process according to the invention more closely.

5 In the following examples water means always completely deionized water.

Example 1

10 In a polymerization reactor flushed with nitrogen a mixture of 4 g sodium dodecylsulfate and 263 g water is heated under stirring to 65°C. After attaining the polymerization temperature 28 g of a monomer mixture, under nitrogen, prepared from 40 g glyceryl-cyclocarbonato-methacrylate, 55 g styrene and 72 g butyl-acrylate, is stirred into the aqueous emulsifier solution. After emulsifying, 15 g of an initiator solution, gassed with nitrogen, prepared from 0.15 g 2,2-azobis-(2-aminopropane)-dihydrochloride ("Wako 15 Chemicals, Inc.") and 35 g water, is added. It is prepolymerized for 15 minutes. Then during 1.5 hours the rest of the initiator solution, and during 3 hours the rest of the monomer mixture, are dropped in from separate funnels. 1.5 hours after the last monomer addition a solution of 0.15 g of the same initiator in 15 g water, gassed with nitrogen, is added to the reaction mixture and the polymerization is continued for another 2 hours. Approx. 0.3 % of a solid coagulate are deposited. The solid content of the polymer emulsion is 34%, the latex 20 particle sizes are between 0.1 -0.4 µm. The thus obtained polymer emulsion shows no viscosity increase and no flocculation after six months.

Example 2

25 In a polymerization reactor flushed with nitrogen a mixture of 3.5 g sodium dioctylsulfosuccinate (Aerosol-OT, "American Cyanamide Co.") and 247 g water is heated to 55°C under stirring. For the start of the polymerization a monomer mixture, gassed with nitrogen, prepared from 31.8 g glyceryl cyclocarbonatometh-30 acrylate, 53 g butyl-acrylate, 70.6 g styrene and 19.8 g methacrylic acid, and 18 g of an initiator solution, gassed with nitrogen, prepared from 0.35 g 2,2'-azobis-(N,N'-dimethyleneisobutyroamidine)-dihydrochloride ("Wako Chemicals, Inc.") and 70.6 g water, are dropped into the emulsifier solution. A milky-white emulsion is formed immediately. After a prepolymerization period of 25 minutes, the rest of the monomer mixture and the rest of the initiator solution are dropped into the reaction mixture during 2 hours from separate funnels. The polymerization is continued for another 2 hours. Approx. 1% of a solid coagulate is deposited. The solid 35 content of the polymer emulsion is 33.5%, the latex particle sizes are between 0.5 - 0.8 µm. The emulsion stays unchanged after half a year.

Example 3

40 In a polymerization reactor flushed with nitrogen a mixture of 5 g sodium dodecylsulfate and 260 g water is heated under stirring to 72°C. After attaining the polymerization temperature a solution, under nitrogen, of 0.3 g 2,2'-azobis-(N,N'-dimethyleneisobutyroamidine)-dihydrochloride ("Wako Chemicals, Inc.") in 40 g water and a monomer mixture, under nitrogen, of 20 g glyceryl-cyclocarbonato-methacrylate, 72 g butyl-acrylate, and 75 45 g methylmethacrylate are dropped into the emulsifier solution during 2 hours from separate funnels. An emulsion is formed immediately. 3 hours after the end of the monomer addition a mixture of 0.05 g of the initiator mentioned above and 8 g water is added to the reaction mixture and the polymerization is continued for another 3 hours. Approx. 0.6% of a solid coagulate are deposited. The solid content of the polymer emulsion is 35%, the latex particle sizes are between 0.2 - 0.5 µm. The emulsion stays unchanged after six 50 months.

Example 4

55 A solution of 120 g of a polyurethane prepolymer W 790 (70% solution in methylethylketone, isocyanate content 1.7%, 0.03 g COOH/g polymer, manufacturer: Reichhold Chemie AG, Vienna) and 450 g water-free acetone is heated to reflux under nitrogen. A mixture of 5.5 g glycerincyclocarbonate and 50 g water-free acetone is dropped into the boiling solution during 2 hours. After another 2 hours 0.5 g dibutyl-tin-dilauroate are added. The mixture is then heated under reflux until no free isocyanate groups can be detected (approx. 3 hours, control by IR spectroscopy). The solid content of the modified cyclocarbonate containing polyurethane 60 solution is 14.4%. After cooling to 40°C a mixture of 5.2 g 2-(dimethylamino)-propanol-2, 1.3 g water and 50 g acetone is added to this solution and stirred for 1 hour. The obtained polymer solution is then dropped during 1 hour into 450 g vigorously stirred and at 40°C kept water, while at the same time volatile parts are distilled off under vacuum (approx. 15 mbar). The opaque dispersion after 2 hours contains practically no more organic 65 solvent. The cyclocarbonate modified polyurethane emulsion has a solid content of 15.3% and remains

Example 5

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In a polymerization reactor, flushed with nitrogen, a mixture of 5 g Aerosol 22 (35% by weight in water, American Cyanamide Co.), and 125 g water is heated to 65°C under stirring. After reaching the polymerization temperature, 10 ml of a solution of 2,2'-azo-bis(2-amidinopropane)-dihydrochloride (WAKO-Chemicals Co.) in 40 g water gassed with nitrogen and 25 ml of a monomer mixture from 21 g glyceryl cyclocarbonatomethacrylate, 22.7 g acrylonitrile, 21.8 g styrene and 21.8 g n-butyl acrylate gassed with nitrogen are dropped from separate dropping funnels into the emulsifier solution. An emulsion is formed immediately. The temperature rises to 70°C. 25 minutes after the start of the polymerization the remaining amounts of initiator solution and monomer mixture are dropped in continuously during 2 hours. Afterwards, the polymerization is continued for another 3 hours at 65 to 70°C. The solid content of the obtained polymer emulsion is 33.8% according to a polymer yield of 97.7%. Less than 1% coagulate is deposited to the stirrer and to the walls of the vessel.

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Example 6

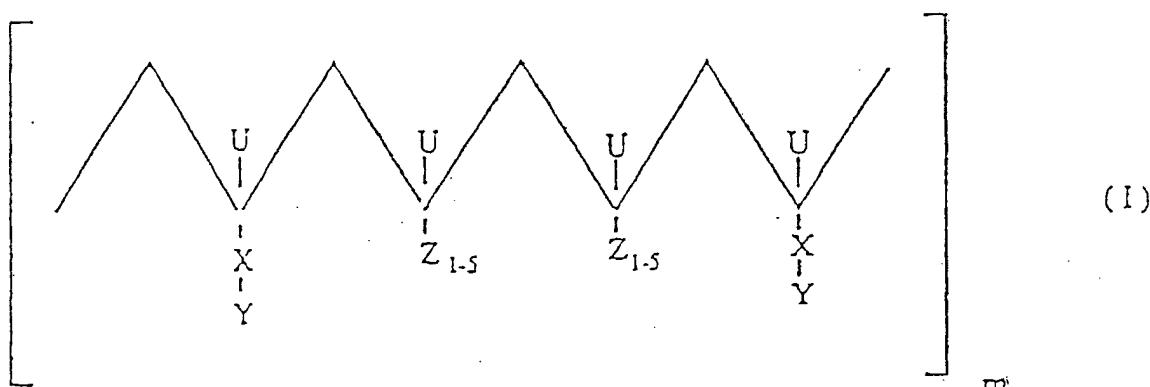
In a polymerization reactor flushed with nitrogen a mixture of 4.4 g Aerosol A 22 (35% by weight in water, American Cyanamide Co.), and 125 g water is heated to 50°C under stirring. After reaching the polymerization temperature a solution of 1.76 g ascorbic acid in 50 g water gassed with nitrogen and a mixture of 22:3 g glyceryl cyclocarbonatomethacrylate, 33.1 g n-butyl acrylate, 33.1 g styrene and 1.16 g tert.-butylhydroperoxide (70% in water) gassed with nitrogen are dropped from separate dropping funnels during 35 minutes into the emulsifier solution of 50°C. An emulsion is formed immediately. The polymerization is continued for another 2 hours. The polymer yield is 100% with a solid content of the stable emulsion of 33.3% by weight.

Claims

1. Storage stable aqueous emulsion

wherein

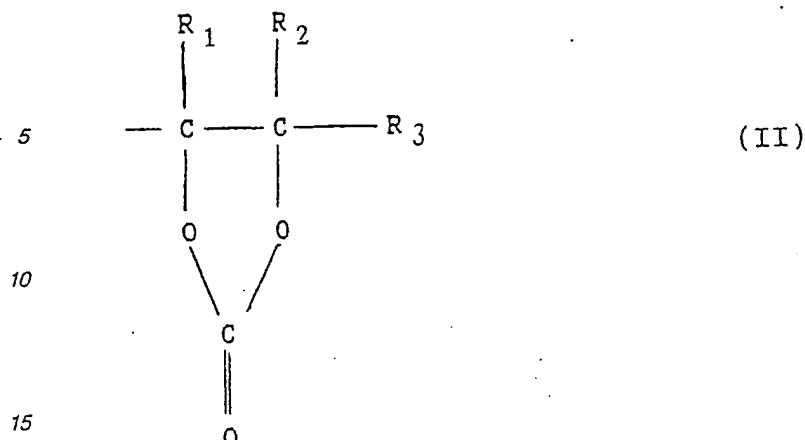
said emulsion has a solid content of 5 to 80%, advantageously of 25 to 60%, of emulsified polymers in which the main chain consists of partially substituted -CH₂- groups, according to the general formula (I)



wherein U, X, Z₁ to Z₅ have the following meaning:

U = -H, -CH₃, -COOH, -COOCH₃, -CONH₂, -COO-(CH₂)₁₋₄-X-Y

Y = 2-oxo-1,3-dioxolan-4-yl group of the general formula (II)



in which

R₁, R₂ and R₃ each stand for a hydrogen atom or a substituted or unsubstituted methyl group, wherein the residues can be identical to each other or different.

20 X = $-\text{O}-\overset{\text{II}}{\text{C}}-(\text{CH}_2)_{1-4}-$, $-\text{S}-\overset{\text{II}}{\text{C}}-(\text{CH}_2)_{1-4}-$, $-\text{O}-\overset{\text{II}}{\text{C}}-\text{NR}-(\text{CH}_2)_{1-4}-$

where R = H or alkyl,

Z₁ = $-\text{COO}-(\text{CH}_2)_{0-17}-\text{CH}_3$

Z₂ = phenyl-, meta-, ortho-, para-substituted alkylphenyl groups

25 Z₃ = $-\text{COOH}$

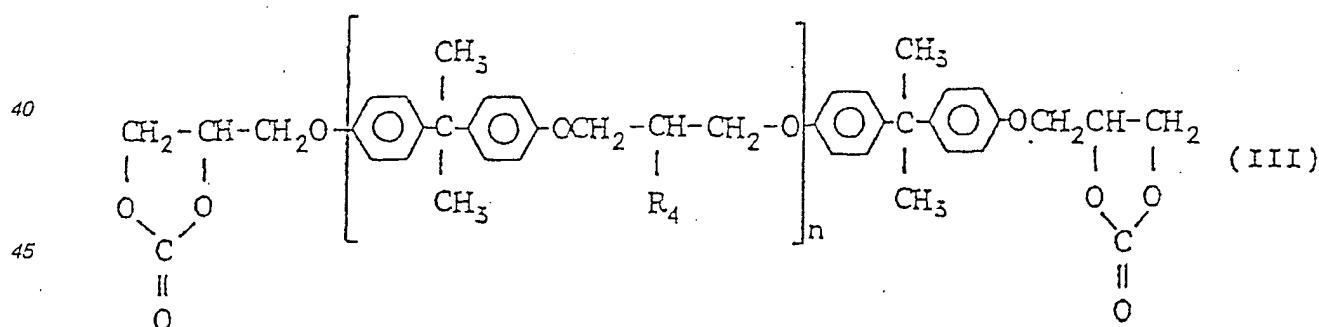
Z₄ = $-\text{CN}$, $-\text{COO}-(\text{CH}_2)_{1-4}-\text{N}(\text{alkyl})_2$, $-\text{COO}-\text{CH}_2-\text{CH}_2-\text{N}(\text{alkyl})_2$

Z₅ = $-\text{COO}-(\text{CH}_2)_{1-4}-\text{OH}$, $-\text{COO}-(\text{CH}_2-\text{CH}_2\text{O})_{1-10}-\text{CH}_2-\text{CH}_2-\text{OH}$

in which at least two groups -X-Y- per macromolecule have to be present and the groups Z₁ or Z₂ can be present either alone or Z₁ in combination with Z₂ to Z₅, wherein the sum of the weights portions of the polymerizable starting materials with the groups -X-Y and Z₄ in the emulsified macromolecule must not exceed the value of 70 % by weight.

2. Storage stable aqueous emulsion wherein

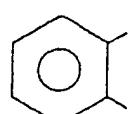
said emulsion has a solid content of 5 to 80%, advantageously of 25 to 60%, of emulsified polymers in which the main chain is built according to the general formula (III) and the secondary OH groups are fully or partially substituted by R₄



50 wherein n stands for a number from 1 to 10 and R₄ is a half ester groups of the general formula (IV)

$-\text{O}-\overset{\text{II}}{\text{C}}-\text{B}-\overset{\text{II}}{\text{C}}-\text{OH}$ (IV)

with B being equal to $-(\text{CH}_2)_{2-3}-$, $-\text{CH}=\text{CH}-$, or



60 which is fully or partially neutralized with alkali metal ions or with secondary or tertiary amines.

3. Storage stable aqueous emulsion

wherein

said emulsion has a solid content of 5 to 80%, advantageously of 25 to 60%, of emulsified polymers in which the main chain is built according to the general formula (V)

wherein

T = -(CH₂)₂₋₁₀, -(CH₂-CHR)₁₋₅, or -CH=CR (with R = H, alkyl, ortho-, meta-, para-substituted phenyl groups)

5 S = -(CH₂)₂₋₁₂, -(CH₂-CHR-O-)₁₋₂₀, or -CR_{4-m}[(CH₂-CHR-O-)₁₋₂₀]_m with R = H or alkyl, and m = 1 to 4

Q = tri- or tetrasubstituted phenyl groups with one or two additional -COOH groups

Y = 2-oxo-1,3-dioxolan-4-yl group according to the general formula (II)

in which at least 2 groups Y per macromolecule have to be present and in which the free acid groups in emulsion are fully or partially neutralized with alkali metal ions or with secondary or tertiary amines.

10 6. Storage stable aqueous emulsion as claimed in anyone of the claims 1 to 5,

wherein

said emulsion has a solid content of 30 to 40% of emulsified polymers.

15 7. A process for the manufacture of a storage stable aqueous emulsion according to anyone of the claims 1 to 5,

wherein

solvent-free or solvent-containing polymers, which on average bear per macromolecule at least two 2-oxo-1,3-dioxolan-4-yl groups of general formula (II) above as side or end groups, are emulsified in water.

20 8. A process for the manufacture of a storage stable aqueous emulsion of emulsified polymers as claimed in claim 1,

wherein

said polymers are manufactured by aqueous emulsion copolymerization of

a) 1 to 60% by weight of a polymerizable compound containing group (II) with

25 b) 20 to 95 weight % of non-functional esters of acrylic or methacrylic acid in the alcohol residue, and optionally

c) 5 to 75 weight % of aromatic vinyl compounds

d) 1 to 40 weight % of hydroxyl group bearing α, β -ethylenic unsaturated compounds

e) 1 to 20 weight % of α, β -unsaturated mono- or dicarboxylic acids

f) 1 to 40 weight % of polar-aprotic acrylic or methacrylic monomers with 1 to 12 carbon atoms and at least one nitrile- or dialkylamino group in the side group,

wherein

30 the sum of the weight portions a) and f) must not exceed the value of 70 weight % in the polymer, with an ionic, preferably anionic emulsifier of a high hydrophilic value and a water-soluble initiator or a redox-initiator system in the temperature range between 0° and 70°C.

35 9. A coating material

comprising one or several storage stable aqueous emulsion according to anyone of claims 1 to 7 with or without usual additives.

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